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<p>(54) Title: SYNTHETIC CLAY MINERALS</p> <p>(57) Abstract</p> <p>A process for the production of a synthetic clay mineral having a hectorite structure but containing no or little lithium, in which process potassium is present in the reaction mixture during the precipitation or during the hydrothermal treatment, gives process advantages in the time taken to prepare the reaction mixture and in the ability to use a relatively low autoclave pressure for a lithium-free hectorite. The potassium-containing lithium-free or low lithium synthetic hectorite product can be dispersed to give a particularly clear dispersion and may be compatible with food usage.</p>		

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SYNTHETIC CLAY MINERALS

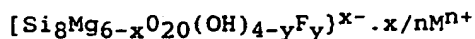
This invention relates to synthetic clay minerals and to a process for the production of such minerals.

The naturally occurring clay mineral, hectorite, is a layered silicate material in which each layer comprises a central
5 octahedrally co-ordinated magnesia plane bound to two adjacent tetrahedrally co-ordinated silica planes by the sharing of oxygen atoms. Some of the magnesium atoms in the octahedral layer are substituted by lithium atoms to give an overall negative charge to the structure which is balanced by
10 exchangeable cations. Some of the hectorite hydroxyl groups are usually substituted by fluorine atoms. Natural hectorite generally occurs in an impure state intimately associated with other minerals such as, for example, dolomite or calcite and unless otherwise specified is supplied in the form of a purified
15 or beneficiated product. Even in that form natural hectorite has relatively poor rheological properties and /or ion exchange properties in aqueous systems.

The synthesis of a material resembling purified natural hectorite in respect of its structure and having rheological properties of
20 a similar level to those of natural hectorite was reported in

Clays and Clay Minerals, National Academy of Science, National Research Council Publication 8, (1960), 150-169, by W T Granquist et al. This material was relatively poorly crystalline and offered no appreciable advantage in use over natural hectorite while being considerably more expensive to produce.

The synthesis of clay-like minerals having a structure shown by x-ray diffraction analysis and by cation exchange capacity measurements to resemble natural hectorite and having a composition similar to that of natural hectorite but with a fluorine content much higher than that of any naturally occurring hectorite is described in UK Patent Specification No 1054111. This synthetic mineral was reported to have rheological properties greatly improved over those of naturally occurring hectorite and this improvement was ascribed to its high fluorine content. The synthetic method described in UK Specification No 1054111 is to combine in an aqueous medium and in the presence of the lithium and fluoride ions the constituent providing the magnesium ions with the constituent or constituents providing the silicon (as silicate), hydroxyl and sodium ions, to form a coprecipitated slurry, and hydrothermally treating the slurry for at least 10 to 20 hours at atmospheric pressure. The synthetic hectorite-like material produced according to this process was reported to have a composition according to the general formula:



wherein x is a numerical value greater than 0 and less than 6, y is a numerical value at least equal to 1 and less than 4, M is a cation and n is the valency of M. This material had an x-ray diffraction pattern characteristic of a smectite structure as described in, for example, "The x-ray identification and crystal structure of clay minerals", The Mineralogical Society (1961), G Brown.

The synthesis of clay-like minerals of the smectite type including minerals having a structure shown by x-ray diffraction to be similar to that of hectorite is described in UK Patent Specification No 1213122. This synthetic hectorite had a
5 composition which included preferably up to 1.45 atoms of lithium per 8 atoms of silicon, and had improved rheological properties without containing fluorine. The synthetic method described in this specification is to coprecipitate the constituents of the clay mineral at a pH above 8.0 and to heat the resulting slurry,
10 without washing it free of soluble salts, under elevated pressure.

UK Patent Specification No 1213122 also describes the synthesis of a lithium-free hectorite by the use of increased pressure during the hydrothermal treatment in contrast to the pressures
15 down to 10 bars which might be used in the production of the lithium-containing material. There has been a long-standing belief in the art that it is necessary to use high superatmospheric pressure and high temperature to produce lithium-free synthetic hectorite having acceptable rheological
20 properties and this is reflected in the process used in the examples of the production of lithium-free products in this specification. In those examples the use of an autogenously generated pressure of 38.2 bars (temperature 250 °C) for 1/2 hour to 1 hour gave a synthetic hectorite product having a plastic
25 viscosity of 12 cp, a Bingham Yield Value of 95 dynes/cm² and a cation exchange capacity of 0.55 m eq/g while the use of an autogenously generated pressure of 68 bars (temperature 286 C) for 4 hours gave a product having a plastic viscosity of 13 cp, a Bingham Yield Value of 152 dynes/cm² and a cation exchange
30 capacity of 0.63 m eq/g. On a production scale, the necessity to use equipment capable of operating at higher pressures than would be necessary for the production of normal lithium-containing material would involve the economic disadvantage of increased capital costs.

Due to their excellent rheological properties synthetic hectorites are effective thickeners in a variety of applications. There are requirements in the food industry for thickeners which could be filled by synthetic hectorite thickeners provided that
5 they are acceptable on other criteria. In the case of lithium-containing synthetic hectorite it is possible that there could be some degree of lithium release on exposure to stomach acids. Lithium-free synthetic hectorite would not be subject to this problem and would be potentially acceptable to the food industry
10 subject to any necessary approvals. The provision of an economic process for the production of lithium-free synthetic hectorite or saponite is therefore of industrial utility.

The present invention relates to a new or improved process for the production of a synthetic clay mineral having an x-ray
15 diffraction pattern and composition indicative of a hectorite. The process is particularly suitable for the production of a synthetic hectorite or saponite containing a relatively reduced quantity of lithium or no lithium. The invention also relates to a new or improved composition of matter
20 comprising a synthetic hectorite or saponite clay mineral. Where in the following Description and Claims reference is made to a synthetic hectorite, this should be interpreted as including any materials alternatively known as synthetic saponites. It is understood that there is interchange of the two terms in the art.

25 According to one aspect thereof the present invention provides a process for the synthesis of a clay mineral having an x-ray diffraction pattern and composition indicative of a lithium-free hectorite by forming a precipitate containing the constituents of the synthetic hectorite, hydrothermally treating the precipitate
30 to cause crystallisation of the synthetic hectorite and recovering the crystallised synthetic hectorite the process being characterised in that there is present during the precipitation or the hydrothermal treatment a dissolved source of potassium cations. According to a further aspect thereof the present
35 invention provides a process as last above described wherein the synthetic hectorite contains octahedral lithium in a reduced quantity, preferably less than 0.06 atoms of lithium per 8 atoms of silicon, and the quantity of lithium compound present during

the precipitation or hydrothermal treatment is controlled accordingly.

The synthesis of hectorite containing from 0.06 to 0.44 atoms of octahedral lithium and containing 0.02 or 0.04 atoms of potassium, each per 8 atoms of silicon and the latter apparently introduced as an incidental ingredient in the reactants, is disclosed in Clays and Clay Minerals, Vol.37, No.3, 248-257, 1989. The lower level of lithium indicated above was due to a very low level of structural incorporation from the synthesis liquor due to the use of the very low hydrothermal treatment temperature of 150°C. The present invention is primarily directed to lithium-free synthetic hectorites and this aspect of the invention is distinguished on this basis as well as on the basis of the intentional use of potassium. Some of the benefits of the present invention will apparently be attained in the synthesis of hectorite containing a small but detectable quantity of lithium and this is therefore within the scope of the present invention. This aspect of the invention is distinguished by the exclusion of the level of lithium disclosed in the Clays and Clay Minerals paper and/or by limitation to a quantity of potassium above that disclosed in that paper.

The present invention further provides a new or improved composition of matter comprising a synthetic clay mineral having an x-ray diffraction pattern and composition indicative of a lithium-free or low lithium content hectorite characterised in that the composition of the clay mineral includes potassium.

The potassium cation is generally regarded as having a relatively large ionic radius in comparison with the other alkali metal cations which are usually utilised in synthetic clays. Lithium and sodium cations, for example, have calculated ionic radii of 0.60 and 0.95 Angstroms whereas the potassium cation has a radius of 1.33 Angstroms on the same basis. It has nevertheless been

found possible to include the potassium cation in the synthetic hectorite structure according to the present invention.

According to the present invention it has been found that the autoclave pressure used need often be no more severe when used in
5 the production of a clay in which the quantity of lithium is reduced or in which lithium is absent than those used in the production of the corresponding lithium clay. The present invention also enables the time taken to establish the reaction mixture to be reduced. Lithium carbonate is slow to dissolve
10 whereas potassium carbonate, which may be used as a reactant, dissolves quickly at room temperature. The rate of addition of the other reactants used in the clay synthesis may also be higher according to the invention. The fully crystalline product of the invention may be relatively slow to disperse, unless this is
15 rectified by the use of a longer hydrothermal treatment but, when dispersed, may give a higher degree of clarity than the corresponding lithium clay. A major potential utility of the product of the invention is as a thickening agent in foods since it need contain no elements such as lithium which could be
20 objectionable in foods. The product may also be free of fluorine if desired.

The process of the present invention will now be more particularly described with reference to the production of a lithium-free fluorine-free synthetic hectorite clay although it
25 is understood that the reactants may be varied to include those elements. It is particularly understood that the benefit of the invention may be obtained at least in part in embodiments where there is partial replacement of lithium by potassium in the reaction mixture.

30 A reaction mixture may be established using the sequential precipitation method described in US Patent Specification No 4049780 although other known techniques such as the coprecipitation method of UK Patent Specifications No 1054111 or 1213122 are not excluded from the ambit of the invention. These

methods involve strongly alkaline precipitation conditions. Less alkaline processes such as those in which the reactants are in the main in the oxide or hydrous oxide form are also not excluded.

- 5 Without any intention to limit thereto the present invention may be put into practice as follows. The source of potassium may first be dissolved in water. The potassium compound used may be any water soluble potassium compound which does not introduce undesired ions into the reaction mixture, for example potassium
- 10 carbonate of which the carbonate ion may be removed from the reaction mixture as CO_2 by heating the suspension of synthetic clay precursor under atmospheric pressure, potassium hydroxide, potassium fluoride if fluorine is to be included in the synthetic clay product, or a suitably water soluble potassium silicate.
- 15 The dissolution of the potassium compound may be accomplished at ambient temperature with agitation in only a few minutes, for example from 5 minutes to 60 minutes, although a somewhat elevated temperature may be used if required. A water soluble magnesium compound such as, for example, magnesium sulphate or
- 20 magnesium chloride, may then be dissolved in the solution of the potassium compound. This may be accomplished relatively quickly, for example in from 5 to 60 minutes at a somewhat elevated temperature of, for example, 30 to 80 degrees C with agitation. The combined solutions are then treated by the addition of a
- 25 suitable base to precipitate the magnesium content thereof. The base may be sodium carbonate or alternatively sodium hydroxide or ammonia. Suitably the temperature is maintained as in the previous addition step. A suitable water soluble silicon compound is then added to the suspension of the magnesium
- 30 compound which contains sufficient excess base to precipitate the silicon to form the clay precursor. Alternatively additional base may be added for that purpose. A suitable silicon compound is sodium silicate, sodium silicofluoride or other silicon compounds used for this purpose in the art. If fluorine and/or
- 35 lithium are to be included a suitable fluorine and/or lithium

compound is preferably added prior to the precipitation of the silica. Suitable fluorine compounds have already been identified above and suitable lithium compounds may be lithium sulphate or chloride.

- 5 The quantities of the various reactants used in the process are selected according to the formula of the desired synthetic hectorite since this may be varied considerably for example by varying the silicon/magnesium ratio. The magnesium compound is preferably present in the reaction mixture in less than 6,
10 preferably less than 5.9 and possibly down to 4.5 atoms per 8 atoms of silicon. There is often substantially complete incorporation of the magnesium content of the medium. It is a preferred feature of this invention that there be a deficiency of magnesium in the hectorite structure, not filled, or fully
15 filled, by lithium atoms thereby leaving anionic vacancies in the structure and increasing the charge of the hectorite structure. As stated above the lithium compound, if present, is in a restricted quantity only. The potassium compound is suitably used in a sufficient quantity to give a product containing at least
20 0.03, greater than 0.04, or at least 0.1, and up to 0.5 or even up to 1.5 atoms per 8 atoms of silicon. The actual quantity used is preferably in an excess over that required to provide the theoretical composition of the clay, for example a 25% to 200% excess. The sodium compound is preferably used in a similar
25 excess to achieve precipitation. The concentration of the reactants is preferably sufficient to give a concentration of the synthetic clay product of at least 3% and possibly up to 10% by weight subject to any limitations deriving from the need to wash the product.
- 30 The precipitated clay precursor obtained as a suspension as above described is preferably aged at elevated temperature and at atmospheric pressure for, for example 30 minutes to 4 hours to develop the initial clay structure. The temperature during this stage is preferably at least 60°C. It is understood that some or

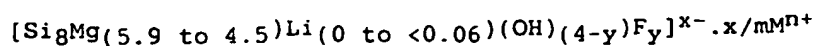
all of the above operations, particularly the precipitation of the silica, may be conducted at superatmospheric pressure and elevated temperature if desired as described, for example, in European Patent Specification No 088372.

- 5 The synthetic hectorite precursor so formed may be treated hydrothermally at superatmospheric pressure and elevated temperature, for example under the autogenous pressure developed in an autoclave at a temperature of above 150°C preferably above 180°C and up to 300°C but preferably at not more than 220 degrees
10 C until the crystallisation of the synthetic hectorite has been brought to completion for example preferably for from 4 hours to 12 hours or, to augment dispersion properties, up to 24 hours.

The suspension in aqueous liquid of the synthetic hectorite product which results from the hydrothermal treatment may be
15 filtered or otherwise dewatered to recover the product which may then be washed to remove soluble salts and dried.

The product of the present invention may have a typical hectorite-like x-ray diffraction pattern and composition and may be dispersed in water to give rheological properties similar to
20 previous synthetic hectorites of corresponding composition as regards their silicon/magnesium ratio and their lithium content and a particularly good degree of optical clarity. The potassium content of the product may be at least in part exchangeable, for example with sodium cations. Potassium-form synthetic hectorite
25 and more particularly, without limitation, that containing a reduced quantity, or no, lithium and/or fluorine, or that in which a proportion of the potassium is non-exchangeable, is claimed herein as a new or useful industrial product.

There is more particularly provided by this invention a synthetic
30 hectorite having an x-ray diffraction pattern characteristic of a hectorite and a composition according to the general equation:



wherein "M" is one or more cations of the same or different valencies "n" said cations including potassium in at least 0.03K⁺, preferably greater than 0.04K⁺ and particularly preferably at least 0.1K⁺ and up to, preferably, 0.5K⁺ or even up to 1.5K⁺, "x" is a numerical value equal to the unit cell charge and "y" is a numerical value at least equal to 1 and less than 4. A typical product had a cation exchange capacity of 0.403 m. eq./g. and showed viscosity characteristics similar to those of lithium-free hectorite produced in the absense of potassium by the prior art high pressure process.

Certain embodiments of the invention will now be more particularly described with reference to the following non-limiting examples.

In the Examples, of which Examples 1 to 13 and 16 are according to the invention, a standard preparation (Example 2) is shown to be reproducible by repetition in Examples 1, in which the autoclave time was extended to 18 hours to demonstrate the optimisation of the dispersion properties of the product, and 3 and is modified, mainly but not exclusively, by the variation in the quantity of potassium which is included in examples 4 to 13 and by the variation in certain of the reactants, for comparative purposes, in Examples 14 to 16. In Example 14 the standard preparation was varied only by the omission of the potassium compound and in Example 15 the potassium compound was replaced by an equivalent quantity of sodium carbonate. Both of these Examples gave a product which gave a reasonable dispersion time but formed a cloudy gel which took several days to clear in comparison with the immediately clear gels of Examples 1 and 2. In Example 16 the sodium carbonate precipitant was replaced by potassium carbonate there being therefore two additions of this compound.

The Examples and their results are summarised in Tables 1 and II of which Table I sets out the hydrothermal treatment conditions and the product analysis and Table II sets out the product properties. Figures I and II represent x-ray diffractograms, Figure I being derived from the product of the standard preparation and Figure II being derived from the corresponding preparation in which all the potassium which was used is replaced by lithium. The product to which Figure 2 relates is therefore a standard lithium hectorite. Both diffractograms are typical of a synthetic hectorite product.

The standard preparation was conducted as follows. Potassium carbonate (4.91g, 0.035M) was dissolved in normal mains water (254.03g) and stirred for 15 to 20 minutes in a 2 litre glass vessel at ambient temperature. The temperature was then raised to 60 degrees C and magnesium sulphate heptahydrate (102.04 g, 0.41M) was added while continuing the stirring. The solution became cloudy. Stirring was continued for 20 to 30 minutes. Sodium carbonate was then added slowly to the solution, with continuing stirring, using a peristaltic pump over a 25 to 30 minute period. This caused the magnesium values to precipitate. Sodium silicate solution ($\text{Na}_2\text{O}:\text{SiO}_2:\text{H}_2\text{O} = 36.81:11.14:77.9$ by weight) was then added in a similar manner over a 45 to 50 minute period. The temperature of the suspension was then raised to 96 degrees C and maintained at that temperature for 2 hours to remove excess carbon dioxide and initiate the formation of the clay structure. The suspension was allowed to cool to 60 degrees C and was then autoclaved for 6 hours at a temperature of 208 to 215 degrees C and a pressure of 17 to 18.36 bars. The suspension was allowed to cool to ambient temperature and was then filtered through a Whatman No 541 filter paper under suction and washed with 2.5 to 3.5 litres of warm demineralised water. The filter cake was then oven dried at a temperature of 110 degrees C and was then milled to give 50 to 60g of product.

The milled product was subjected to x-ray diffraction examination, which showed a typical hectorite structure, was analysed for its Si, Mg, Na and K content and was tested in aqueous dispersion for its dispersion and gelling properties and its conductivity. The rate of dispersion (minutes) was determined by making up 2%wt of the product in a dilute (0.12%wt) tetrasodium pyrophosphate solution circulating the solution through a 1 cm diameter cell and noting the time taken to reach a given standard of optical clarity (0.200 absorbance) using a UV spectrophotometer. The time to gel (minutes) was determined by noting the time taken for a 2% aqueous dispersion of the product in a 1.136g/litre Na₂SO₄ solution to thicken sufficiently to suspend a metal ball to a given extent. The gel clarity was determined visually and the gel strength was determined by a standard penetration method. The conductivity of a 2% dispersion of the product was measured in microsiemens.

The following short headings are used in the Tables:

AP	Autoclave Pressure (bars)
AT	Autoclave Temperature (degrees C)
20 H2O	Qty. Wash Water (litres)
K+/-	% wt Variation of Qty. Potassium
OD	Optical Dispersion Time (mins)
GS	Gel Strength (g)
25 GT	Gelling Rate (mins)
CON	Conductivity (um)
CLAR	Visual Clarity of Gel

The elemental analysis and ratios are expressed as wt% calculated as the oxides.

30 The oxide quantities derived from the product of the standard preparation corresponded to a product containing, per 8 atoms of silicon, 5.4 atoms of magnesium 0.47 atoms of sodium and 0.03

atoms of potassium. It is possible that some of this potassium may be present in non-exchangeable form.

It may be concluded from the Examples summarised in the following Tables that the presence of potassium may give a product which
5 disperses to give a particularly clear dispersion which may be produced using a relatively low autoclave temperature and, if a somewhat extended autoclave duration is used, a good rate of dispersion despite containing a relatively low quantity, or no, lithium. The novel potassium hectorites of the invention may
10 show an optical dispersability as measured herein of below 10 and a gelling rate as measured herein of below 30.

TABLE
I

EX. NO.	AP	AT	H2O	K+/-	Si	Mg	Na	K
1	18.36	211	2.5	0	61.06	28.33	3.74	0.34
2	17.34	208	2	0	59.74	28.58	3.17	0.37
3	17.34	208	2	0	57.37	26.44	3.52	0.45
4	18.02	211	2.5	-10	60.04	28.78	3.53	0.32
5	18.02	211	2.5	-20	59.91	28.33	3.71	0.31
6	18.36	211	3.5	-30	60.01	28.05	3.61	0.32
7	17.17	211	3.5	-40	60.52	29.07	3.37	0.22
8	18.02	211	3.5	-50	57.35	27.93	3.67	0.17
9	17.68	208	2	10	57.09	26.34	3.54	0.48
10	17.68	209	3.5	20	58.55	27.4	3.44	0.49
11	17.17	214	3.5	30	58.33	27.46	2.78	0.46
12	17.68	211	3.5	40	56.48	25.42	4.05	0.63
13	17.17	214	3.5	50	57.05	16.03	2.36	0.43
14	14.01	208	2.5	-100	59.21	27.86	3.67	0
15	17.01	208	2.5	Na	58.81	27.94	3.53	0
16	17.01	208	2.5	K	58.98	28.13	0.71	3.2

TABLE II

EX. NO.	OD (min.)	GS (g)	GT (min.)	Clarity	Conductivity (μ m)
1	2.3	23.7	23	Clear	900
2	7.5	31.1	30	Clear	718
3	5.2	34.1	30	Cloudy	975
4	10	33.9	30	Clear	764
5	19.1	35.8	30	Cloudy	774
6	7.5	33.8	30	Clear	570
7	8	30.3	30	Clear	755
8	9.4	34.9	30	Clear	397
9	9.1	37.1	30	Clear	1160
10	7.4	32.2	30	Clear	1210
11	11.3	31.2	30	Clear	758
12	13.5	36.6	30	Clear	1415
13	16.4	34.9	30	Clear	405
14	7.1	36.1	30	Cloudy	950
15	11.1	24.1	30	cloudy	835
16	4.3	37.1	30	Clear	536

Claims.

1. A process for the synthesis of a clay mineral having an x-ray diffraction pattern and composition indicative of a hectorite which is lithium-free or contains less than 0.06 atoms of lithium per 8 atoms of silicon the process comprising forming a
5 precipitate containing the constituents of the synthetic hectorite, hydrothermally treating the precipitate to cause crystallisation of the synthetic hectorite and recovering the crystallised synthetic hectorite the process being characterised in that there is present during the precipitation or the
10 hydrothermal treatment a dissolved source of potassium cations.
2. A process for the synthesis of a clay mineral having an x-ray diffraction pattern and composition indicative of a hectorite and containing a quantity of lithium which is less than which is sufficient to fill the vacant sites in the octahedral layer the
15 process comprising forming a precipitate containing the constituents of the synthetic hectorite and including a reduced quantity of lithium compound effective to control the lithium content of the hectorite product within the specified limit, hydrothermally treating the precipitate to cause crystallisation
20 of the synthetic hectorite and recovering the crystallised synthetic hectorite the process being characterised in that there is present during the precipitation or the hydrothermal treatment a dissolved source of potassium cations in a quantity effective

to give at least 0.1 atoms of potassium per 8 atoms of silicon in the synthetic hectorite product.

3. A process as claimed in claim 1 wherein there is present during the precipitation or the hydrothermal treatment a quantity
5 of a dissolved potassium compound effective to give at least 0.03 atoms of potassium per 8 atoms of silicon in the synthetic hectorite product.

4. A process as claimed in claim 1 wherein there is present during the precipitation or the hydrothermal treatment a quantity
10 of a dissolved potassium compound effective to allow a reduction in the temperature and/or the pressure of the hydrothermal treatment for the production of a specific synthetic hectorite.

5. A process as claimed in any preceding claim wherein the hydrothermal treatment is conducted under the autogenous pressure
15 generated at a temperature of from 180°C to 250°C in a sealed reactor.

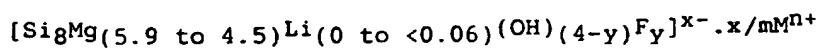
6. A process as claimed in claim 5 wherein the autogenous pressure is that generated at a temperature of about 208 to 215°C.

20 7. A synthetic hectorite which is lithium-free or contains less than 0.06 atoms of lithium per 8 atoms of silicon characterised in that it has a content of potassium.

8. A synthetic hectorite as claimed in claim 7 containing at least 0.03 atoms of potassium per 8 atoms of silicon.

25 9. A synthetic hectorite containing at least 0.1 atoms of potassium per 8 atoms of silicon.

10. A synthetic material having an x-ray diffraction pattern characteristic of a hectorite and a composition according to the general equation:



5 wherein "M" is one or more cations of the same or different valencies "n" said cations including potassium in at least 0.03 atoms per 8 atoms of silicon, "x" is a numerical value equal to the unit cell charge and "y" is a numerical value at least equal to 1 and less than 4.

10 11. A synthetic hectorite as claimed in claim 7 or claim 9 and substantially as described herein.

12. A process for the production of a synthetic hectorite as claimed in claim 1 or claim 2 and substantially as described herein.

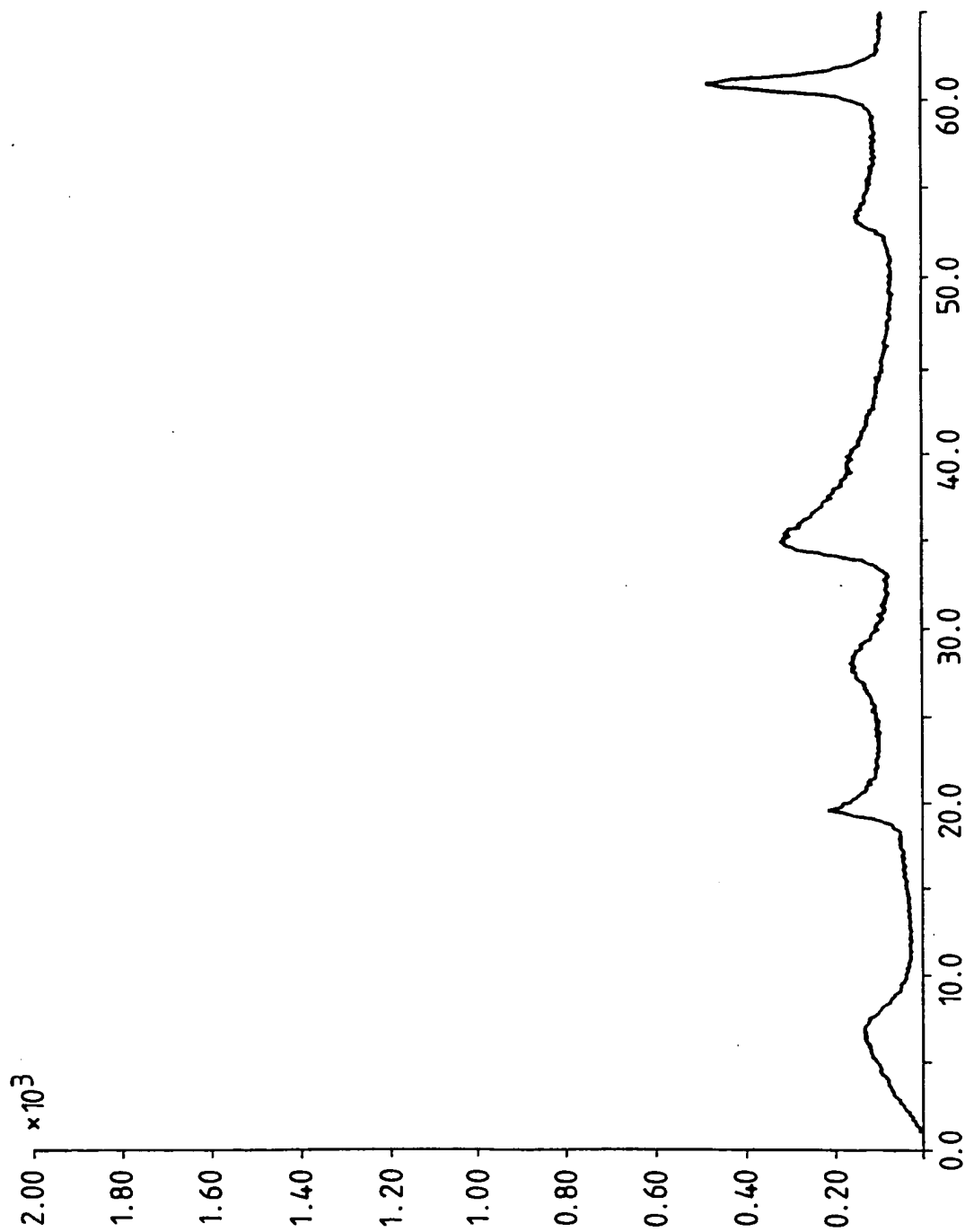
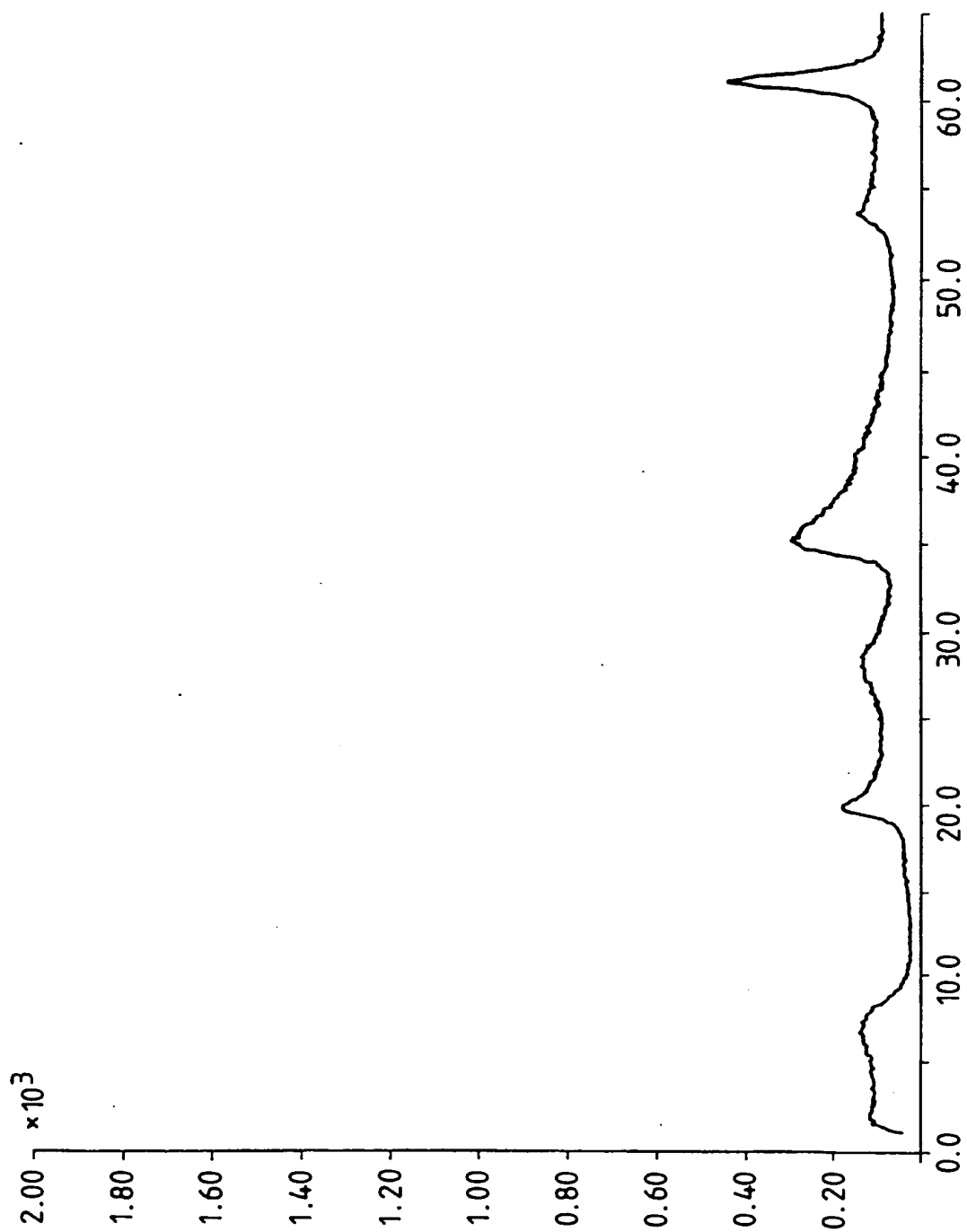


Fig.1

*Fig. 2*

INTERNATIONAL SEARCH REPORT

International Application No
PCT 94/00025

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C01B33/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 100, no. 10, 5 March 1984, Columbus, Ohio, US; abstract no. 70753e, page 140 ; see abstract & JP,A,58 194 736 (AGENCY OF INDUSTRIAL SCIENCES AND TECHNOLOGY) 12 November 1983 ---	1,3-5, 7-10
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

31 May 1994

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

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